Structure, Electrical Resistivity and Superconductivity of Low-alloyed γ -U Phase Retained to Low Temperatures by Means of Rapid Cooling

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Abstract The γ -U phase alloys can be retained down to low temperatures with less required alloying concentration by using the splat-cooling technique with a cooling rate better than 10^6 K/s. Doping with 15 at.% Mo, Pt, Pd, Nb leads to a stabilization of the cubic γ -U phase, while it requires much higher Zr concentrations (≥ 30 at.% Zr). All U–T splats become superconducting with T_c in the range of 0.61–2.11 K. A good agreement of the experimentally observed specific-heat jump at T_c with that from BCS theory prediction was obtained for U-15 at.% Mo consisting of the γ -U phase with an ideal *bcc* A2 structure.

KEY WORDS: Crystal structure; Electrical resistivity; Metallic system; Superconductivity

1 Introduction

1.1 Cubic γ -U Phase

Uranium ($Z = 92$) is a main component of the most nuclear fuels. Fundamental physical properties of elemental uranium have been investigated thoroughly for the orthorhombic α -U phase (space group *Cmcm*) [1, 2], since only this phase is stable at and below room temperature. The superconductivity of (natural) uranium was first discovered at 1.3 K in 1942 [3]. Most recent data have reported $T_c = 0.78$ K [4, 5]. However, no signature of the

superconductivity was found down to 0.02 K at ambient pressure in good-quality single crystals of uranium, although the charge-density-wave (CDW) states [5] were found to be developed fully at low temperatures in those crystalline uranium specimens [6].

The γ -U phase with a body-centered cubic structure (space group *Im $\bar{3}m$*) is stable at high temperatures between (1049 ± 2) and 1408 K [1, 2]. It can be retained to the room temperature by alloying with Zr, Nb, Mo, Pd, Pt, etc. [7]. Mo has a large solubility in U (≈ 35 at.%) and thus is considered as a good candidate to stabilize γ -U. For instance, the single-phase γ -U alloy has been reported for U-8 wt% Mo (U-16.5 at.% Mo) under normal furnace cooling conditions [8].

The large interest in stabilization of γ -U phase alloys has mostly come from the viewpoint of metallurgy. In the late 1970s, massive research programs were launched in the USA to develop the low enriched uranium (LEU, $<20\%$ ^{235}U) fuels [9, 10]. The research showed that the γ -U–Mo alloys were the most promising candidates for LEU fuels; e.g., they have a higher stability under irradiation and they are more resistant against swelling (than α -U alloys) [11, 12]. Besides, they are much more stable phase for manufacture and greater fissile load [13]. U–Mo alloys were also found to be the top

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performers among many U-based fuel alloys in the screening tests. U-10 wt% Mo was selected for the US reactors, while many European reactors continue to use the U-7 Mo [10]. This percent (7–10 wt% Mo) in the metallic U is enough to obtain the γ -U phase stability.

1.2 Use of Ultrafast Cooling in Stabilizing the Cubic γ -U Phase

The $5f$ electronic states in many uranium-based compounds are generally close to the verge of localization, which brings up fascinating many-body physics from the fundamental research viewpoint. In this respect, it is necessary to determine the basic thermodynamic properties of the less-known γ -U phase alloys. Except of old reports from 1960s on the superconductivity of the γ -U phase around 2 K in water-quenched U–Mo and U–Nb alloys [14, 15], no more detailed data exist for the γ -U alloys.

We have been interested in stabilization of γ -U alloys and characterization of their fundamental electronic properties, especially their superconductivity. It was shown earlier that the rapid quenching (with a cooling rate of about 10^5 K/s) of certain alloys from the melting point could lead to a formation of new metastable phases and/or amorphous solid phases [16]. Indeed, the splat-cooling technique has been used for searching novel microstructure or amorphous uranium [17]. Recently, using ultrafast cooling from the melt to room temperature, we can retain the cubic γ -U phase in U– T alloys. In our equipment, the molten metal is dropped between two colliding massive copper anvils, yielding a cooling rate better than 10^6 K/s [18]. Another advantage of this technique is that it can work with small amounts of material (200–300 mg). We can then proceed with characterization of low-temperature properties of the γ -U phase alloys. Starting with Mo alloying, we succeeded to suppress the γ -U phase with about 11 at.% Mo [18, 19].

In the present work, we concentrate on stabilization of the γ -U phase by a combination of ultrafast cooling and other T alloying (T = Pt, Pd, Nb, Zr). We have also investigated the low-temperature properties of the obtained splat-cooled U– T alloys, in particular their superconductivity. Some results are compared with those obtained earlier for U–Mo splats.

2 Experimental

U– T alloys (T = Mo, Pt, Nb, Zr) with low- T contents (up to 30 at.%) were prepared using natural U (2N8 purity or better) and T element (3N8 or better) by arc melting on a copper plate in argon atmosphere. The splat-cooled sample was prepared from the alloy ingot by splat-cooling technique (using the HV splat cooler from Vakuum Praha) and had a shape of irregular disk with a diameter of approx.

20 mm and a thickness of 100–200 μm , as shown in Fig. 1. More details of preparation of the splats have been reported earlier [18]. Throughout our work, the T content is given in the atomic percent (at.%).

The crystal structure of the splat-cooled alloys (splats) was investigated by X-ray diffraction (XRD) using the Bruker D8 Advance diffractometer with Cu- $K\alpha$ radiation. The resistivity and specific heat measurements were carried out in the temperature range 0.3–300 K by means of standard techniques, such as closed-cycle refrigerator system (CCR) and Quantum Design Physical Properties Measurement System (PPMS) described earlier [18]. For investigations around the superconducting transitions, we performed those measurements in applied magnetic fields up to 7 T. Additional phase purity analysis was performed by scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) analyzer. The splats show a homogeneous distribution of the alloying elements with concentrations corresponding to the nominal ones. Some C, O and Cu contamination was observed for the splats after preparation. Cu on the surface comes evidently from the Cu anvils of the splat cooler. Also, C and O are related to the surface (resulting from segregation) [19]. Electron backscattering diffraction (EBSD) analysis has been employed to study the microstructure and the texture of several splats (next section).

3 Results and Discussion

3.1 Stabilization of the Cubic γ -U Phase in U–Mo Splats

We have investigated thoroughly the crystal structure of U–Mo splats with Mo concentration of 0 (pure U splat), 1,

Fig. 1 Photograph of the bulk ingot with a mass of ≈ 300 mg (*left*) prepared by the arc furnace and the resulting splat-cooled sample disk (*right*) produced by HV splat cooler

2, 4, 6, 10, 11, 12, 13, 15, 17 at.%, in order to determine precisely the minimal Mo concentration necessary for obtaining pure cubic γ -U phase. Details of our investigations of crystal structure and phase stability have been reported earlier [18, 19]. For a necessity of a comparison with other U-based splats, we summarize briefly the main outcome obtained on U–Mo splats below:

- The orthorhombic α -U phase disappeared, and the γ -U phase developed fully in the alloys with ≥ 11 at.% Mo. A pure cubic γ -U phase without any distortion or diffusion is revealed only for U-15 at.% Mo (and also for U-17 at.% Mo) (see Fig. 1 in Ref. [19]).
- The stable γ -U alloys were obtained in the as-formed state without any additional sample treatment. Moreover, no aging or phase transformation/decomposition was observed when exposed to air. They show even very good resistance against any hydrogen absorption in the hydrogen atmosphere with the pressure below 2.5×10^5 Pa (2.5 bar).

The effect of the splat cooling can be seen in a better capability in retaining the *bcc* type of structure for lower (by several at.%) Mo concentrations. The reason can be, besides preventing the $\gamma - \alpha$ transformation, also avoiding the inhomogeneity of the Mo distribution in the γ -phase, which may appear due to the narrow bi-phase region between liquidus and γ -U with Mo. On the other hand, the splat cooling does not affect crystallinity: The materials do not turn amorphous.

EBSD analysis has been performed on several U–Mo splats, since this technique can give the direct information about spatial distribution of the phases and orientation of the grains. For this technique, a high surface quality is a prerequisite and special procedures have to be applied because of the tendency to oxidize rapidly in air [20]. In general, the first step of the sample preparation for all methods is mechanical polishing. The specimens were mechanically polished on SiC grinding papers (up to 4000 grid) using water and then coarse polished with using 3 and 1- μ m diamond abrasive on a nylon lap with a diamond suspension. To reveal the microstructure of the sample surface and to remove the surface oxide as the last step of preparation, Ar ion milling in the precision ion polishing system (PIPS) was performed. As an alternative technique, in situ focused ion beam (FIB) milling in chamber of SEM could be employed. Our experience shows that ion milling is a convenient way for preparing U-based surfaces. However, the surface of the specimen after the preparation procedure depends strongly on the sample compositions. Namely, the properties of γ -U surface (e.g., with more Mo doping) are very different from those of mostly α -U ones which was found in low-doped U alloys. Therefore, the preparation method should be still optimized for different

U alloys. Earlier published EBSD results for pure U and U-15 at.% Mo splats [18] corroborated the XRD data. We succeeded to get also good EBSD map for other γ -U(Mo) alloys such as U-12 at.% Mo (Fig. 2), revealing an equigranular grain structure without twinning and preferred crystallographic texture. The grain size is similar to that in U-15 at.% Mo alloy (between 3.1 and 5.2 μ m). We notice here that the XRD data revealed the γ^0 -U phase in this splat. But the equipment cannot resolve such a small structure variation, i.e., a small tetragonal distortion of the γ -U phase. Therefore, the structure was identified as the γ -U phase. The important point is that for this splat, no any evidence for α - or α -U related phases was observed in EBSD map, confirming the XRD data. Some isolated areas (shown as a black area in Fig. 2) were identified to be UC, confirmed by the Kikuchi pattern. Despite of our strong effort and a hard work on lower doped Mo alloys, no good EBSD map has been yet obtained, since it was difficult to get the free-oxidized surface which could diffract. The EBSD mapping on low Mo doping and other T-doping alloys is in the progress.

3.2 Crystal Structure of U–*T* Alloy Splats (*T* = Pt, Pd, Nb, Zr)

We have extended our studies to the splat-cooled U-based alloys with other *T* metals. We note here that while it is quite easy to produce the splats of U–Mo, U–Nb and U–Zr alloys in a wide range of Mo/Nb/Zr content, the similar procedure applied on U–Pd and U–Pt alloys turned out trickier. Namely, it is quite difficult to produce the splat disk for the Pd and Pt concentrations exceeding 5 at.% [21]. Our investigations revealed that the XRD patterns, the resistivity drops and T_c values are very similar for the same alloying level whether Pt or Pd is used. Thus, we focus our attention on the U–Pt splats, trying to get a larger set of the splats with different Pt concentrations (1, 2, 5, 10 and 15 at.%), while only two Pd-containing splats were investigated for comparison.

The XRD patterns of U–Pt splats in the as-formed state are shown in Fig. 3a. For an easier comparison, we display normalized XRD patterns; i.e., the intensity of the most intense reflection around 36° – 37° ($=2\theta$) was set to 1. The patterns are then shifted upwards to provide a better visual comparison. Increasing the Pt concentration leads to merging of several peaks around 36° , suppression of the low-index α -peaks, vanishing of the high-index α -peaks and a development of γ -peaks. The situation is very similar to U–Mo alloys, showing a coexistence of both α - and γ -U phases for splats with less than 10 at.% alloying level. For both U–Pt and U–Pd splats, additional peaks appeared at around 37.6° and 38.9° , i.e., between the $\alpha(002)$ and $\alpha(111)$ peaks. Such peaks are more visible for the Pt than Pd case.

Fig. 2 EBSD crystallographic orientation map **a** and the Kikuchi pattern **b** highlighting the surface microstructure of the splat-cooled U-12 at.% Mo alloy which identified only γ -U phase and UC (small black areas) with no evidence for α -U or α -U-related phases

Their intensity decreases with further increasing Pt/Pd concentration, and they vanish in alloys with ≥ 10 at.% Pt/Pd. We cannot be conclusive on the basis of XRD about the spurious phase; we can only rule out the β -U phase, which has been never found in any splat-cooled U-*T* alloys. The two additional peaks also cannot be associated with the binary U-Pt phase (U-Pt with monoclinic structure of the PdBi type, mP16, space group $P2_1$), which should have the two strongest peaks at 33° and 41° [22]. The XRD pattern of U-15 at.% Pt revealed four characteristic peaks of the γ -type structure [$\gamma(110)$, $\gamma(200)$, $\gamma(211)$ and $\gamma(220)$, respectively, at 36.8° , 53.0° , 65.3° and 78.2°], indicating a stabilization of the cubic γ -U phase. However, unlike U-15 at.% Mo with very narrow γ -peaks indicating the reflections of the fundamental cubic A2 structure, there is a certain broadening for all the γ -peaks in U-15 at.% Pt, similar to that observed in U-13 at.% Mo splat. It is interesting to compare our findings with respective binary phase diagrams. The maximum reported solubility in γ -U of Pt or Pd does not exceed 5 at.% [7, 22–24]. Our results reveal that using the splat cooling we not only retain the bcc phase to low temperatures, but also extend its occurrence for much higher concentrations of alloying Pt/Pd metals.

The normalized XRD patterns of the splat-cooled U-Nb alloys in the as-formed state are shown in Fig. 3b. In general, the increase in the Nb concentration leads to the suppression of α -U reflections and the development of γ -U reflections. It causes the overlap of low-index peaks around 36° , and then the combined peak becomes narrower for 10 at.% Nb. For the U-15 at.% Nb alloy, the splitting of the γ -reflections into doublets was observed for all four prominent γ -peaks. For instance, the $\gamma(110)$ reflection of U-15 at.% Nb splits into doublet located around 36.3° [$\gamma^0(101)$] and 37.0° [$\gamma^0(110)$]. The situation is similar to that of doping with 11–12 at.% Mo which stabilizes the γ^0 -U phase (the body-centered tetragonal structure with the c/a ratio of about 0.98–0.99). In general, our results show a similarity between the U-Nb and U-Mo systems. It is in a good agreement with an earlier observation revealing that the mode of formation of α -, α' - and γ^0 -phase in the U-Nb system is very similar to that observed in the U-Mo system. Moreover, we expect that using ultrafast cooling could reduce the necessary Nb concentration. Indeed, it turned out that the γ^0 -U phase is found to be stabilized by 15 at.% Nb doping, i.e., lower than the minimal content for stabilization of such a phase in water-quenched (16.8 at.% Nb)

Fig. 3 XRD patterns of the as-formed splat-cooled U-Pt alloys **a** and U-Nb alloys **b**. Each curve was normalized to the maximal intensity of the most intense peak at $2\theta = 36^\circ\text{--}37^\circ$ and then shifted upwards with respect to that of pure U splat. The color vertical ticks indicate the main XRD patterns of orthorhombic (blue) and cubic (red) structures and of the surface impurities (black). The four main γ -reflections are also indicated

[25] or in argon-quenched ones (16.2 at.% Nb) [26]. Using a combined arc melting, hot rolling, annealing and water quenching, the γ -U phase was stabilized in U-7 wt% Nb ($\sim$ U-15 at.% Nb) alloy [27].

In the case of the U-Zr system, there is a similar situation to for U-Nb, i.e., the complete miscibility of the high-temperature *bcc* phase. The normalized XRD patterns of the splat-cooled U-Zr alloys in the as-formed state are shown in Fig. 4a. The results illustrate the phase transformation from the α -phase to γ with increasing Zr concentration. Unlike other *T* doping, the $\alpha(110)$ and $\alpha(111)$ peaks still persist for U-11 at.% Zr and U-15 at.% Zr, but become very broad for U-20 at.% Zr and then vanish for U-30 at.% Zr, as shown in more detail in an enlarged scale in Fig. 4b. Existing reports indicate that the single-phase γ -alloys were obtained for Zr concentrations between 25 and 80 at.% [28]. In our case, the γ -U reflections increase visibly with increasing Zr concentration and become dominant for all splat samples with Zr concentrations ≥ 11 at.%. We notice here that U-7wt% Zr ($\sim$ U-15 at.% Zr) alloy prepared by a combined arc melting, hot rolling, annealing and water quenching has revealed still a mixed $\alpha + \gamma$ -U phase [27]. In our case, the single γ -U phase can be considered only for U-30 at.% Zr splat. Moreover, most of the γ -reflections [including the main peak $\gamma(111)$ at 35.9°] are broadened.

At low Zr concentrations, the broadening can be seen in the overlap of the γ -peaks with the α -peaks. But at high Zr concentrations, the contribution from α -peaks was minimized. Thus, the main reason for the peak broadening should be the additional disorder (microstrain) by randomly distributed Zr atoms (less probable due to almost identical atomic size) and/or limited grain size due to splat cooling. This suggestion is confirmed by the fact that the peak broadening increases with Zr concentration. Similar to other splats, UC (111) and UO_2 (111) impurity peaks were observed in the low-angle part of the XRD patterns. These impurities are segregated at the surface of the splats and can be easily removed by the sample scraping; i.e., these impurity peaks are largely reduced after scraping. Narrow peaks of ZrC were observed for U-Zr samples with the most intense reflections ZrC (111) and ZrC (200) at 33.4° and 38.7° , respectively. Traces of carbon are ubiquitous in uranium metal, and it seems that it couples preferentially with Zr when it enters the alloy, and moreover it has a high surface segregation tendency. We also notice that no sign of the phase UZr_2 (δ -phase) was found in XRD patterns even if for the samples with high Zr content (20 and 30 at.% Zr).

For more details, we show in Fig. 5 the comparison of the most intense reflection in XRD patterns at around 37°

Fig. 4 XRD patterns of the as-formed splat-cooled U–Zr alloys shown as normalized ones **a**. The same notations of the color vertical ticks are used as those in Fig. 3. The enlarged low-angle XRD patterns **b**. For U–Zr splats, apart from surface impurities UO_2 and UC, the peaks of spurious ZrC are observed

of as-formed splat-cooled U-15 at.% *T* splats, i.e., with the same amount of 15 at.% *T* alloying. A single sharp γ -peak and no trace of any α -peaks were observed only for U-15 at.% Mo consisting of a pure single *bcc* structure (γ -U phase). The *bcc* structure could be also stabilized in U-15 at.% Pt (combined with ultrafast cooling), but a small trace of α -U phase is still present. Alloying with 15 at.% Nb could stabilize the γ^0 -U phase, but with a larger broadening of γ^0 -peaks, in comparison with those for U-12 at.% Mo splat. We also add to the figure the data for U-30 at.% Zr exhibiting the γ -U phase. The $\gamma(110)$ peak is relocated to lower angles reflecting a lattice expansion. We have also investigated the crystal structure of splats with combined 12 at.% Mo plus 3 at.% Zr alloying, i.e., replacing 3 at.% Mo in U-15 at.% Mo by 3 at.% Zr [U-15 at.% (Mo + Zr)]. A doublet splitting was observed for all γ -peaks. The peaks are quite narrow, similar to those of U-12 at.% Mo. Besides, the most intense doublet assigned to $\gamma^0(101)$ and $\gamma^0(110)$ reflections (at 36.8° and 37.0° , respectively) of U-15 at.% (Mo + Zr) is more symmetric and with roughly equal intensity. In other words, exchanging 3 at.% Mo by 3 at.% Zr doping implies a change from pure *bcc* structure [γ -U phase (in U-15 at.% Mo)] into a body-centered tetragonal structure (γ^0 -U phase).

The lattice parameters estimated for the γ -U phase alloys are given in Table 1. The atomic radius of Nb (1.45 Å), Pd (1.40 Å) and Pt (1.35 Å) was equal or close to that of Mo (1.45 Å), all of which are lower than the nominal atomic radius of U (1.56 Å), while the Zr atomic radius (1.60 Å) is larger [29]. We may consider that replacing some Mo by Zr atoms would induce a tetragonal distortion of the cubic lattice and/or some shifts of the atoms from their ideal A2 sites. We notice here also that the $\gamma(110)$ reflection in U-15 at.% Nb and in U-15 at.% (Mo + Zr) locates at 37.0° , i.e., at the angle similar to that of the pure cubic U-15 at.% Mo alloy, indicating that the *a* parameter of the tetragonal structure in these alloys is similar to that of the *bcc* structure of U-15 at.% Mo. The earlier observation indicated that for the U–*T* alloys, the *a* parameter is not affected visibly by alloying, while the *b* and *c* parameters exhibit some variations. Besides, the atomic radius of Nb is similar to that of Mo. Thus, doping with 15 at.% Nb or exchanging a part of Mo by Zr (3 at.%) should not lead to any visible change of the unit cell. But it is not clear why Nb doping implies much broader doublets than those with Mo doping, despite that Nb is an immediate neighbor of Mo. The $\gamma(110)$ reflection in U-15 at.% Pt is located at a lower angle (36.8°). It indicates that, although the 15 at.% Pt doping leads to a stabilization of the *bcc* structure,

smaller Pt atoms (in comparison with Mo atoms) can lead also to a visible microstrain [broader γ (110) reflection], although the lattice parameter of the two alloys is similar. Doping with Zr, i.e., with larger atoms, certainly leads to a large expansion of the lattice. The relative increase in the lattice (Δa) is estimated to be about 3% for 30 at.% Zr alloying.

Fig. 5 Comparison of the most intense reflection in XRD patterns of U–*T* splats with 15 at.% *T* alloying [*T* = Mo, (Mo + Zr), Pt, Nb] in the as-formed state. Sharp γ -phase peaks and no trace of α -phase peaks were observed for only U-15 at.% Mo splat

3.3 Superconductivity in the U–*T* Splats Stabilized in the Cubic γ -U Phase

3.3.1 Electrical Resistivity and Superconductivity in U–Mo Splats

For a brief summary of the change of the temperature coefficient in sputter-cooled U–*T* alloys with increasing *T* content in the normal state in the temperature range 3–300 K, we show in Fig. 6 the temperature dependence of the (normalized) electrical resistivity of U–Mo splats (the data were reported separately earlier [18, 30, 31]). We concentrate on analyzing the two limit cases (Fig. 6a), which reveal a striking difference in the pure U splat (consisting of α -U phase) and the U-15 at.% Mo splat (consisting of the γ -U phase only). The pure U splat exhibits a quadratic temperature dependence below 50 K and then an almost linear dependence up to 300 K, i.e., with a positive temperature coefficient ($d\rho/dT > 0$). Unlike such a common metallic behavior, for U-15 at.% Mo, the resistivity weakly decreases with increasing temperature in the normal state in the whole temperature range, i.e., with a negative temperature coefficient ($d\rho/dT < 0$). The temperature dependence of the resistivity of other U–Mo splats lies between such the two limits. In other words, increasing the Mo content leads to a change from metallic ($d\rho/dT > 0$) to nonmetallic *T* dependence ($d\rho/dT < 0$). Besides, while U–Mo alloys consisted of both α - and γ -phases (with $< 10\%$ Mo doping) have still positive $d\rho/dT$, all γ -phase U–Mo alloys (with $\geq 11\%$ Mo doping) have the negative $d\rho/dT$. We suggest that a large disorder effect plays an important role in the sputter-cooled alloys, similar to a strong disorder observed, e.g., in some (superconducting) amorphous system [32], Heusler alloys [33] and disordered heavy-fermion compound URh₂Ge₂ [34]. The reason for the negative slope can be seen in the weak localization, i.e., a quantum interference effect (e.g., the anomalous

Table 1 Summary of low-temperature properties of U–*T* splat alloys: resistivity values at 300 K and at 4 K ($\rho_{300\text{ K}}$, $\rho_{4\text{ K}}$), superconducting transition temperatures (T_c) determined from the $\rho(T)$ jump and/or from the specific heat $C(T)$, the width of the superconducting

transition in the resistivity (ΔT_ρ), the Sommerfeld coefficient of electronic specific heat (γ_e) and Debye temperature (Θ_D). The structure and lattice parameters (*a*, *c*) are also given

<i>T</i> content (at.%)	Type	<i>a</i> , <i>c</i> (Å)	$\rho_{300\text{ K}}$ ($\mu\Omega\text{ cm}$)	$\rho_{4\text{ K}}$ ($\mu\Omega\text{ cm}$)	T_c (K) [$\rho(T)$]	ΔT_ρ (K)	T_c (K) [$C(T)$]	γ_e [mJ/(K ² mol)]	Θ_D (K)
Pure U	α		53	14	1.24	0.20	0.65	11.0	179
15% Mo	γ	3.441	89	95	2.11	0.02	2.11	16.0	139
15% Pt	γ	3.469	164	166	0.95/0.61	0.08/0.04	0.75	19.5	145
15% Nb	γ^0	3.435 (<i>a</i>) 3.565 (<i>c</i>)	83	86	1.90	0.15	1.90	13.7	153
15% (Mo + Zr)	γ^0	3.431 (<i>a</i>) 3.482 (<i>c</i>)							
30% Zr	γ	3.543	75	73	0.81	0.08	0.60	11.8	165

Fig. 6 Temperature dependence of electrical resistivity (in zero field) of U–Mo splats in the normal state **a** and around the superconducting transition temperature **b**. For an easier comparison, the curves were normalized to respective resistivity values at $T = 300$ K and at $T = 4$ K. All U–Mo splats with the γ -U phase (≥ 11 at.% Mo doping) have a negative temperature coefficient ($d\rho/dT < 0$). The pure single γ -U phase U-15% Mo splat has a highest critical temperature ($T_c = 2.11$ K) and sharpest resistivity drop

dispersion of the conduction electrons) occurring in strongly disordered systems [35]. In our case, there is certainly still some extra contribution to the disorder produced by ultrafast cooling, affecting the grain size, but the fact that $d\rho/dT < 0$ found in all U–Mo alloys with *bcc* structure reveals a dominant role of strong conduction electron scattering on randomly distributed U and Mo ions.

All investigated U–Mo splats become superconducting at low temperatures. The superconducting transitions revealed by abrupt resistivity drops in zero magnetic field are shown in Fig. 6b. We focus firstly on the data for the two limits: the pure U splat and the U-15 at.% Mo splat. The transition is manifest as a single drop at $T_c = 1.24$ K and 2.11 K, respectively [18, 30]. We remind here a very small width of the transition $\Delta T_\rho = 0.02$ K observed for U-15 at.% Mo, while a wider transition $\Delta T_\rho = 0.2$ K was found for pure U splat. However, unlike a λ -type anomaly for U-15 at.% Mo, the superconducting transition in pure U splat was revealed only as a small feature around 0.65 K in the specific heat [18]. It is an evidence against the bulk nature of superconductivity. It can be understood only a small fraction of the sample becomes superconducting, and as it has to form a 3D network, it must be related to the grain boundaries. For other γ -U alloys, such as U-11 at.% Mo and U-12 at.% Mo, the superconducting transition also appears as a single resistivity drop, although broader than that in U-15 at.% Mo. We pay particularly attention to the superconducting transition in the U-6 at.% Mo splat [21]; i.e., the intermediate range of Mo doping consisted of both α - and γ -U phases. The phase coexistence is reflected by a flat but still a metallic type overall temperature dependence ($d\rho/dT > 0$). In the low- T range, the resistivity starts to decrease rapidly below 1.6 K, which has to be interpreted as emergence of a small amount of superconducting phase. This decrease ends in an abrupt drop into the zero

resistance state at $T_c = 0.78$ K. The obtained results show that there are two different superconducting phases in the U-6 at.% Mo splat, (we have to assume the coexisting α and γ -U phase), each of which exhibits its own superconductivity. We speculate that the superconductivity of the α -phase is restricted to surface of the grains, but not forming the complete 3D network as the phase is not contiguous, which succeeds to reduce the total resistivity of the composite structure, but has a very little impact on the specific heat. The lower T_c may be associated with the γ -U phase, as it revealed by a sizeable anomaly in the specific heat [21]. We cannot, however, exclude that the higher T_c belongs to the γ -U phase, if that would represent only a very small fraction, assuming that the α -U phase with Mo can have a bulk superconductivity in which Mo prevents the CDW formation.

3.3.2 Superconductivity in U–T Splats ($T = \text{Pt, Pd, Nb, Zr}$) with γ -U Phase

As next step, we focus on a comparison of the resistivity behavior of all splat-cooled U– T alloys ($T = \text{Pt, Pd, Nb, Zr}$) crystallized in the γ -U structure. The temperature dependence of the resistivity of these alloys in zero field and in the temperature range of 3–300 K is shown in Fig. 7a. The resistivity values at 300 K and 4 K are given in Table 1. The $\rho(T)$ curves of U-15 at.% Mo and U-15 at.% Nb splat are quite similar. Besides, the residual resistivity ρ_0 (ρ_4 K) and the resistivity at room temperature ($\rho_{300\text{ K}}$) are also similar (see Table 1). For the U-15 at.% Pt splat, although the resistivity values are twice higher, the relative change of the resistivity in U-15 at.% Pt [the $\rho/\rho_{300\text{ K}}$ (T) curve] is very similar to that of U-15 at.% Mo (as well as U-15 at.% Nb). Namely, from room temperature down to temperature just above the superconducting

transition, the electrical resistivity exhibits a negative temperature coefficient ($d\rho/dT < 0$). For U-30 at.% Zr revealing the γ -U phase, the negative slope does not develop yet. Instead, we found a very small (close to zero) but still positive slope of the temperature dependence in this splat. We like to mention that a negative temperature coefficient ($d\rho/dT < 0$) was indeed reported for U–Zr system, but for sample with 70 at.% Zr [36]. We suggest that the negative slope can be also observed for U–Zr splats, but certainly for higher Zr concentrations than 30 at.%. The low-temperature $\rho(T)$ dependence of U-15 at.% T ($T = \text{Mo, Nd, Pt}$) splats measured in zero field is shown in Fig. 7b. For comparison, we also show in the same figure the data for pure U splat as well as those for U-30 at.% Zr splat (consisted of γ -U phase). In all cases, a very sharp resistivity drop was observed at T_c . The sharpest superconducting transition for all investigated γ -U phase alloys was observed in U-15 at.% Mo ($\Delta T_\rho = 0.02$ K). U-15 at.% Nb becomes superconducting at the superconducting transition temperature $T_c = 1.90$ K, revealing as a single sharp drop at T_c with a transition width $\Delta T_\rho = 0.15$ K. It is noted that U-15 at.% Nb has the γ^0 -U structure. Except of a small difference in the T_c values, the resistivity drop in U-15 at.% Nb is very similar to that of other splat alloys consisting of γ^0 -U structure (with 11–12 at.% Mo). The superconductivity in U-15 at.% Pt was characterized by a sharp drop at $T_c = 0.61$ K with a very small transition width $\Delta T_\rho = 0.04$ K. Despite of a similarity in the crystal structure (γ -U) and lattice parameter between U-15 at.% Mo and U-15 at.% Pt (resulted from alloying with elements with a similar atomic radius), U-15 at.% Pt becomes superconducting at much lower temperature. Besides, an extra feature was observed at 0.95 K with a transition width $\Delta T_\rho = 0.08$ K. The origin of this extra drop is still unknown. More detailed investigations of the superconducting phase transition in

U-15 at.% Pt are in progress. We notice here, even if for the splat-cooled U-5 at.% Pt alloy consisting of a mixed α -U and γ -U phase, the superconducting phase transition is revealed by only a single resistivity drop [21]. Our study shows that double drops are also observed in the U-15 at.% Pt bulk alloy (the precursor of the splat-cooled sample). U-30 at.% Zr exhibits a superconducting transition which is revealed by a single drop at $T_c = 0.81$ K with a transition width $\Delta T_\rho = 0.08$ K.

Applying external magnetic fields, the superconducting transitions shift toward lower temperatures, as expected. The estimated values for critical magnetic fields at zero temperature ($\mu_0 H_c$) and the critical slopes at T_c of the H_{c2} versus T curves [$-\mu_0(dH_{c2}/dT)_{T_c}$] for selected U–Mo splats are reported earlier [18, 19]. In Table 1, we list only the values for pure U and U-15 at.% Mo splat, for a comparison with other T -doping splats.

Applying external magnetic fields, the superconducting transitions shift toward lower temperatures, as expected. The estimated values for ($\mu_0 H_c$) and [$-\mu_0(dH_{c2}/dT)_{T_c}$] are in the range of 2–7 T and 2–4 T/K (see Table 1), respectively. These values are close to that found for the strongly interacting Fermi liquid superconductor U₆Fe [$-\mu_0(dH_{c2}/dT)_{T_c} = 3.42$ T/K] [37] as well as within the limit for the extreme high-field A15 and Chevrel-phase superconductors $2 \text{ T/K} \leq [-\mu_0(dH_{c2}/dT)_{T_c}] \leq 8 \text{ T/K}$ [38]. One difference is that for those splat-cooled γ -U alloys, the T_c values are lower than 2.2 K, while Chevrel-phase superconductors have much higher T_c (>10 K).

3.3.3 Specific-Heat Anomaly at the Superconducting Phase Transition of U–T Splats

The temperature dependence of specific heat, $C_p(T)$, has been studied for selected splats over the whole temperature range, including both the low- T and high- T parts for

Fig. 7 Temperature dependence of the normalized electrical resistivity in zero field of splat-cooled U–T splats having the γ -U phase compared with that of pure uranium splat **a**. All the alloys with 15 at.% T doping ($T = \text{Mo, Nb, Pt}$) have a negative $d\rho/dT$, except for U-30 at.% Zr having a positive one. Superconducting phase transitions indicate by the abrupt resistivity drops in the range of 0.61–2.11 K **b**

characterizing the superconducting behavior as well as the electronic and phonon contribution. The Sommerfeld coefficient of electronic specific heat (γ_e) and the Debye temperature (Θ_D) can be estimated from the C_p/T versus T^2 plot in the normal state [$C_p/T = \gamma_e + \beta T^2$; $\beta = 1944/(\Theta_D)^3$ for C_p in J/(mol K)]. The estimated values are given in Table 1. A clear evidence of an increase in density of states at the Fermi level for γ -U is observed only for U-15 at.% Mo, as shown by an enhancement of the γ_e value by Mo doping [$\gamma_e = 16$ – 18.8 mJ/(K² mol) U for U-15 at.% Mo, in comparison with that for pure U $\gamma_e = 11$ mJ/(K² mol) U]. It is ascribed to the increasing atomic volume and higher U–U spacing. The enhancements of the γ_e value and the softening of the lattice (revealed by reduction in Debye temperature) are found to be smaller for Nb and Zr alloying.

The temperature dependence of the specific heat and its field variations have been performed down to 0.3 K for selected splat-cooled U–T alloys. The jump in the specific heat at T_c within the BCS theory in the weak coupling approximation is:

$$\Delta C = 1.43 \gamma_e T_c.$$

We estimated the height of the experimentally observed specific-heat jump (ΔC) and then compared to the estimated BCS values by using the γ_e and T_c values determined from our experiments.

In Fig. 8, we show the C – T curves in zero field for the two limits: the pure U and U-15 at.% Mo splat. Only a very small feature related to the superconducting transition was revealed at 0.65 K in the specific heat for the pure U splat. The results suggest that only a small fraction of the sample is really superconducting. For U-15 at.% Mo splat (consisted of single γ -U phase with ideal *bcc* A2 structure), a pronounced λ -type specific-heat anomaly was observed. The height of the experimentally observed specific-heat jump (ΔC) is in a good agreement with that estimated from BCS theory (see Fig. 5 Ref. [30]). Such a robust BCS-type superconductivity culminating for U-15 at.% Mo revealed that it might be in analogy with that of U₆Fe [37]. For other U–Mo splats with lower Mo contents (<15 at.%), a broader peak with a smaller (but nonnegligible) specific-heat jump was observed close to the superconducting transition temperature T_c defined from the resistivity measurements. The experimentally estimated jump for instance for U-6 at.% Mo splat amounts to only about 55% of the BCS value [21]. The specific heat of other U–T splats consisted of γ -U phase measured down to 0.3 K in zero magnetic field was shown also in Fig. 8. Only a weak and broad bump with a small height was observed in $C(T)$ curve of U-15 at.% Nb. Although the crystal structure, the resistivity jump and T_c value of this splat are similar to that of U-12 at.% Mo splat, much a larger peak was observed for U-12 at.% Mo in the

Fig. 8 Specific-heat anomalies related to the superconducting phase transition for selected U–T splats. A pronounced λ -type specific-heat anomaly was observed only for U-15 at.% Mo splat consisting of single γ -U phase with ideal *bcc* A2 structure

$C(T)$ curve. The specific heat peak related to the superconducting transition in U-30 at.% Zr splat is visible at T_c determined from the resistivity jump, revealing that the superconductivity in this splat is a real bulk effect.

We notice here also that in the context of the stability of the *bcc* U–T alloys it is interesting to mention their high resistance to hydrogen absorption. While α -U easily absorbs hydrogen even at room temperature and few mbar of H₂ forming UH₃, the U–T alloys with cubic γ -U phase do not absorb hydrogen in the hydrogen atmosphere up to hydrogen pressure of 2.5×10^5 Pa (2.5 bar); i.e., they are highly resistance against hydrogen absorption. We have demonstrated that elevated pressures $p(\text{H}_2) > 2.5$ bar are needed to achieve hydrides of equivalent stoichiometry for U–Mo and U–Zr alloys. The lattice expansion due to hydrogen absorption leads to the disappearance of the superconductivity and the formation of U magnetic moments and their ferromagnetic order. Namely, UH₃, Mo_{0.18} [39] and (UH₃)_{1-x}Zr_x [40] are amorphous 5f ferromagnets with T_c around 200 K, i.e., with the Curie temperature higher than that of α -UH₃ and β -UH₃ (175 K [1, 41]). Preliminary data on other γ -U splats (U-15 at.% Pt and U-15 at.% Nb) indicate that the hydrogen resistance is reproduced as well.

4 Conclusions

The γ -U phase can be retained in the U–T alloys by a combination of ultrafast cooling and doping with 15 at.% T content ($T = \text{Mo, Pt, Nb}$) and 30 at.% Zr content. An ideal *bcc* A2 structure was found only in the U-15 at.% Mo splat. Our results confirm that Mo is the best alloying

element for stabilization of the γ -U structure. It is crucial that using ultrafast cooling we are able to reduce the necessary concentration of the T elements ($T = \text{Mo, Nb, Zr}$); i.e., the γ -U phase can be stabilized by a lower concentration of alloying elements. On the other hand, ultrafast cooling could also extend a higher solubility of Pt and Pd metals in γ -U and retain it to low temperatures. We emphasize again that all splat-cooled alloys were obtained without any additional treatment and they are very stable when exposing to ambient conditions.

All the U– T splats become superconducting with T_c in the range of 0.61–2.11 K. The prediction of BCS superconductivity for the specific-heat jump at T_c was found to be fulfilled in the U-15 at.% Mo among all investigated splats.

The U– T alloys with cubic γ -U phase reveal a high resistance against hydrogen absorption. The hydrogen absorption takes place only in a high hydrogen pressure ($\geq 2.5 \times 10^5$ Pa (2.5 bar)). Hydrogen can be easily desorbed by heating to 500–600 °C in vacuum. Thus, from the technological viewpoint, our study indicates an easy route for producing the γ -U phase in a powder form: by a combination of hydrogenation, followed by crushing of the brittle hydrides and then hydrogen desorption in a vacuum.

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